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COATED PIGMENT AND GRAVURE PRINTING INK COMPOSITION [Hifuku Shori Ganryo Oyobi Gurabia Insatsu Inki Soseibutsu]

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PRINTING INK COMPOSITION

(54) Title of the invention

COATED PIGMENT AN DGRAVURE PRINTING INK COMPOSITION

(57) Summary

<u>Objective</u>: To provide a gravure printing ink composition endowed with excellent viscosity, stability over time, and printed matter luster.

Constitution: A pigment coated with a mixture obtained by adding $0.1 \sim 10$ parts by weight of a water-soluble acrylic polymer to 100 parts by weight (solid content standard) of an aqueous slurry of a monoazo lake pigment obtained by mutually coupling & laking a diazo component obtained by diazoating an aromatic amine in possession of a soluble group and a coupler component as well as a gravure printing ink composition constituted by said coated pigment and a solvent-type gravure printing ink vehicle.

Patent Claims /2

Claim 1

A pigment coated with a mixture obtained by adding 0.1 ~ 10 parts by weight of a water-soluble acrylic polymer to 100 parts by weight (solid content standard) of an aqueous slurry of a monoazo lake pigment obtained by mutually coupling & laking a diazo component obtained by diazoating an aromatic amine in possession of a soluble group and a coupler component.

Claim 2

A coated pigment specified in Claim 1 wherein said diazo component is an aminotoluenesulfonic acid derivative and wherein said coupler component is β -oxynaphthoic acid or β -naphthol.

¹ Numbers in the margin indicate pagination in the foreign text.

Claim 3

A gravure printing ink composition constituted by the coated pigment specified in Claim 1 or 2 and a solvent-type gravure printing ink vehicle.

Detailed explanation of the invention

[0001]

The present invention concerns a monoazo lake pigment with improved fluidity, stability over time, and luster as well as a gravure printing ink composition that uses said pigment.

[0002]

(Prior art)

Monoazo lake pigments obtained by mutually coupling aromatic amines in possession of soluble groups and coupler components provided by β-oxynaphthoic acid or β-naphthol are being used for extensive purposes such as the colorations of printing inks, coating materials, plastics, etc. Attempts have been made, for the purpose of providing transparent & bright colors by using these monoazo lake pigments, to microscopically control the particle shapes of pigments. In a case where such a pigment is used for a solvent-type gravure printing ink, however, the pigment particles become increasingly flocculated as the particle size diminishes, which is problematic in that the ink becomes unusable due to a viscosity gain or gelation. In order to eradicate the aforementioned shortcoming, a pigment composition that uses, as an additive, a condensation product of an aromatic sulfonic acid with formaldehyde has been proposed (Japanese Patent Application Publication Kokai No. Sho 62[1987]-18472 Gazette), although this pigment composition is practically unsatisfactory in that its viscosity reducing effect is tenuous.

[0003]

(Problems to be solved by the invention)

The objective of the present invention is to provide a pigment endowed with excellent viscosity, stability over time, and printed matter luster as well as a solvent-type gravure printing ink composition inclusive of said pigment.

[0004]

(Mechanism for solving the problems)

The present invention concerns a pigment coated with a mixture obtained by adding 0.1 ~ 10 parts by weight of a water-soluble acrylic polymer to 100 parts by weight (solid content standard) of an aqueous slurry of a monoazo lake pigment obtained by mutually coupling & laking a diazo component obtained by diazoating an aromatic amine in possession of a soluble group and a coupler component.

[0005]

The aromatic amines in possession of soluble groups that constitute the diazo component of the present invention may, for example, be instantiated by 2-chloro-4-aminotoluene-5-sulfonic acid, 2-chloro-5-aminotoluene-4-sulfonic acid, 4-aminotoluene-3-sulfonic acid, 4-chloroaniline-3-sulfonic acid, anthranylic acid, 4-chloroanthranylic acid, 2-naphthylamine-1-sulfonic acid, and corresponding sodium salts, etc., and above all, derivatives of aminotoluenesulfonic acids are especially desirable. β -oxynaphthoic acid or β -naphthol is desirable as the coupler component, although it is also possible to use acetoacetoanilides.

[0006]

The monoazo lake pigment of the present invention can be manufactured based on monoazo lake pigment manufacturing methods publicly known in the prior art. In other words, an aromatic amine in possession of a soluble group is diazoated based on an ordinary method, whereas, on the other hand, a coupler component is prepared based on an ordinary method, and after both

components have been coupled based on an ordinary method, the obtained dye is laked by using a pigment laking metal. Such pigment laking metals are instantiated by calcium, barium, strontium, manganese, etc.

[0007]

The present invention is characterized by the coating of the pigment by adding a water-soluble acrylic polymer to a laked pigment slurry. Examples of water-soluble acrylic polymers include an acrylic acid-maleic acid copolymer, polyacrylic acid, polymethacrylic acid, polymaleic acid, isobutylene-maleic acid copolymer, styrene-acrylic acid copolymer, and their sodium salts, potassium salts, or ammonium salts, whereas they are more concretely instantiated by Poise 520, 530, & 540 and Demol EP, P, & LP (manufactured by Kao Co.), Allone T-40 & A-10SL (manufactured by Toa Gosei Kagaku Kogyo Co.), Johncryl 67 & 680 (manufactured by Johnson Polymer Co.), and Durimer AC-10S & AC-20 N (manufactured by Nihon Junyaku Co.). It is desirable for the addition ratio of a case where the water-soluble acrylic polymer of the present invention is used to be designated within a range of 0.1 ~ 10 parts by weight, preferably 1 ~ 5 parts by weight, with respect to 100 parts by weight of the monoazo lake pigment based on the solid content standard. In a case where this ratio is lower than 0.1 part by weight, the effect is minimal, and even in a case where said ratio exceeds 10 parts by weight, the achieve effect is not commensurate with the excess margin.

[8000]

The vehicle resin used for the gravure printing ink of the present invention is selected from among organic solvent-soluble resins. The gravure ink is constituted by $10 \sim 80$ parts by weight of at least one type of resin selected from among gum rosin, wood rosin, tall oil rosin, rosin ester, lime-cured rosin, zincated & cured rosin, maleated rosin, fumarated rosin, nitro cellulose, ethyl cellulose, polyamide, polyurethane, cyclic rubber, and chlorinated rubber, $10 \sim 80$ parts by weight of at least one type of organic solvent selected from among aromatic hydrocarbons, aliphatic hydrocarbons, alcohols, esters, and ketonic solvents (e.g., toluene, xylene, ethyl acetate, acetone, n-hexane,

isopropyl alcohol, etc.), $5 \sim 35$ parts by weight of the coated pigment of the present invention, and 0 ~ 20 parts by weight of a body pigment(s) (e.g., barium sulfate, barium carbonate, calcium carbonate, gypsum, alumina white, clay, silica, silica white, talc, calcium silicate[,] precipitatory magnesium carbonate, etc.) as well as, according to adventitious needs, an auxiliary agent(s) such 1/2 as plasticizers, ultraviolet absorbents, antioxidants, antistatic agents, etc.

[0009]

(Application examples)

In the following, the present invention will be explained in further detail with reference to application examples. In these examples, "parts" and "%" respectively signify "parts by weight" and "wt%."

<u>Application Example 1</u>

After 42.8 parts of sodium 2-chloro-4-aminotoluene-5-sulfonate had been poured into 680 parts of water, the contents were heated and solubilized at 75°C. After 39 parts of a 35% hydrochloric acid had been added to the obtained solution, the mixture was acidolyzed and then spontaneously cooled overnight, and after 480 parts of ice had been further added, the mixture was cooled at an eventual temperature of 0°C. After a solution comprised of 38 parts of water and 12 parts of sodium nitrite had been added to the obtained mixture, the contents were agitated at 3°C or below for 45 min., as a result of which a diazo component was obtained. After 32.5 parts of β-oxynaphthoic acid had been solubilized into a solution comprised of 608 parts of water, 14.3 parts of sodium hydroxide, and 4.3 parts of sodium carbonate, the obtained solution was cooled at an eventual temperature of 15°C, as a result of which a coupler component was obtained. The diazo component was added dropwise to the coupler component over a 10-min. period in order to trigger a coupling reaction, and the contents were agitated over a 60-min. period, as a result of which a dye was obtained. Next, the pH of said dye was adjusted at 7.5 ~ 8.0 by using hydrochloric acid, and

after its temperature had then been elevated to 80°C, 43 parts of barium chloride was added, and the contents were continuously agitated for 30 min., as a result of which the laking reaction was concluded. After 4 parts (solid content standard) of water-soluble acrylic polymer Demol EP had been added to 100 parts of the pigment slurry thus laked, the obtained mixture was agitated, filtered, washed with water, and dried, as a result of which a coated pigment was obtained.

[0010]

Application Example 2

A coated pigment was obtained according to procedures similar to those in Application Example 1 except that 2 parts (solid content standard) of Poise 520 was added, in place of Demol EP, to the same laked pigment slurry.

Application Example 3

A coated pigment was obtained according to procedures similar to those in Application Example 1 except that 2 parts (solid content standard) of Durimer AC-10S was added, in place of Demol EP, to the same laked pigment slurry.

Application Example 4

A coated pigment was obtained according to procedures similar to those in Application Example 1 except that 2.6 parts (solid content standard) of Allone T-40 was added, in place of Demol EP, to the same laked pigment slurry.

[0011]

Comparative Example 1

An untreated pigment was obtained according to procedures similar to those in Application Example 1 except that no water-soluble acrylic polymer was added to the same laked pigment slurry.

Comparative Example 2

A coated pigment was obtained according to procedures similar to those in Application Example 1 except that 2 parts of aromatic sulfonic acid-formaldehyde condensation product Demol N (manufactured by Kao) was added, in place of Demol EP, to the same laked pigment slurry.

[0012]

Application Example 5

After the coupled dye slurry of Application Example 1 had been heated at 50°C, 50 parts of strontium chloride was added to it, and after the contents had been continuously agitated for 30 min., the laking reaction was concluded. After 4 parts of Demol EP had been added to the pigment slurry thus laked, the obtained mixture was heated & agitated at 70°C, filtered, washed with water, and dried, as a result of which a coated pigment was obtained.

Comparative Example 3

A coated [sic: Presumably "An untreated"] pigment was obtained according to procedures similar to those in Application Example 6 [sic: Presumably "5"] except that no Demol EP was added to the same laked pigment slurry.

[0013]

Next, the gravure printing ink compatibilities of coated pigments of the present invention will be shown. The monoazo lake pigment compositions obtained in the respective examples were tested based on the following methods.

(Test methods)

1. Polyamide-nitro cellulose mixture gravure ink

After a mixture of 10 parts of each monoazo lake pigment composition, 80 parts of a polyamide-nitro cellulose mixture varnish, and 10 parts of a solvent (ethyl acetate, toluene, & IPA) had been fed, together with 300 g of 3 mm φ steel balls, into a mayonnaise bottle, the contents were dispersed for 60 min. by using a paint conditioner.

2. Polyurethane gravure ink

After a mixture of 13 parts of each monoazo lake pigment composition, 46 parts of a polyurethane varnish, and 41 parts of a solvent (MEK, toluene, & IPA) had been fed, together with 150 g of 3 mm φ steel balls, into a mayonnaise bottle, the contents were dispersed for 60 min. by using a paint conditioner.

[0014]

The results of the respective gravure tests are shown below.

Table I: Polyamide-nitro cellulose mixture gravure printing inks

| | Ink viscosity | | |
|-----------------------|-----------------------------------|--------------|--------|
| | Immediately after ink preparation | After 1 week | Luster |
| | 6/60 rpm | 6/60 rpm | % |
| Application Example | 175/161 | 200/175 | 93.9 |
| Application Example 2 | 220/205 | 580/484 | 90.5 |
| Application Example | 310/274 | 840/730 | 93.5 |
| Application Example | 225/212 | 660/570 | 90.3 |
| Comparative Example | 2400/952 | 4960/1442 | 85.1 |
| Comparative Example | 880/754 | 3790/1120 | 88.2 |
| Application Example 5 | 560/550 | 940/730 | 86.9 |
| Comparative Example | 4160/1404 | 41500/7800 | 79.5 |

[Note: The viscosity was measured by using a B-type viscometer (unit: cps)]

[0015]

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Table II: Polyurethane gravure printing inks

| | Ink viscosity | | | |
|-----------------------|-----------------------------------|--------------|--------|--|
| | Immediately after ink preparation | After 1 week | Luster | |
| | 6/60 rpm | 6/60 rpm | % | |
| Application Example | 140/113 | 165/125 | 85.3 | |
| Application Example 2 | 155/148 | 580/494 | 83.2 | |
| Application Example 3 | 165/125 | 655/525 | 85.0 | |
| Application Example | 270/216 | 780/690 | 83.8 | |
| Comparative Example | 1790/364 | 21200/4200 | 78.2 | |
| Comparative Example 2 | 730/264 | 5200/2200 | 80.4 | |

(Effects of the invention)

The present invention provides, by coating the pigment surface with a water-soluble acrylic polymer during the manufacture of a monoazo lake pigment, a gravure printing ink composition characterized by excellent viscosity, viscosity stability over time, and printed matter luster.